

Steam Reforming of Biogas over a Rh/Al₂O₃ Catalyst in an Annular Microreactor

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Abstract—The article deals with the catalytic steam reforming of biogas of model composition into hydrogen and carbon monoxide over a Rh/ γ -Al₂O₃ catalyst in an annular microchannel reactor. The reforming of biogas consisting of 60% methane and 40% carbon dioxide in a steam medium has been experimentally investigated under isothermal conditions while activating the reactions on the inner convex wall of the annular microchannel with a thin catalyst layer. The experiments have been performed at a residence time of 0.12 s, reactor temperatures of 750 and 860°C, and a water : biogas molar ratio of 0.8 to 3.1 in the feed. The range of water : biogas molar ratios maximizing the hydrogen yield has been determined for the model biogas. By changing the reactor temperature and water : biogas molar ratio, it is possible to widely vary the hydrogen : carbon monoxide molar ratio in the resulting synthesis gas.

Keywords: steam reforming, hydrogen, biogas, microreactor, Rh/ γ -Al₂O₃ catalyst

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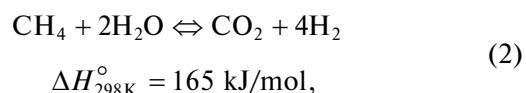
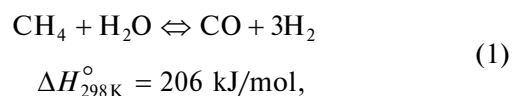
INTRODUCTION

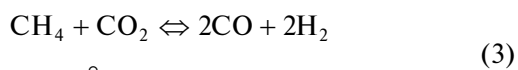
A promising area of contemporary power engineering is hydrogen power engineering, which is based on the production of hydrogen and its direct use in electricity generation in electrochemical converters and in raising the efficiency of combustion of conventional fuels [1]. Hydrogen possesses a variety of valuable properties, including a high combustion rate, a large effective octane number, and wider flammability limits in air compared to those of methane and gasoline. Hydrogen can be considered as a multipurpose, environmentally friendly energy carrier usable in any heat engine and electric power plant. There are many ways of producing hydrogen. These include water electrolysis, plasma chemical oxidation of methane, and coal gasification, but particular attention is deserved by catalytic hydrocarbon oxidation processes, which have a high energy efficiency and are widespread in industry [2]. Possible oxidizers in the catalytic oxidative reforming of methane are steam, carbon dioxide, oxygen, and mixtures of these gases in various proportions. The synthesis gas resulting from methane reforming can be used as a source of hydrogen and as a feedstock in the manufacturing of various chemical and petrochemical products (ammonia, methanol, dimethyl ether, and Fischer–Tropsch synthesis products $n[-CH_2-]$).

Of great current interest is the problem of developing methods for producing synthesis gas from renewable hydrogen sources, such as biogas, which is a gas-

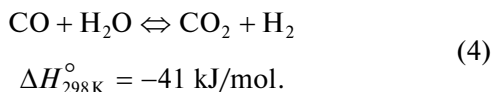
eous product of the anaerobic fermentation of organic matter of various origins (biomass). Hydrogen production from biomass has already become economically profitable owing to biogas being inexpensive and renewable source of energy. Hydrogen production from biomass offers many advantages, including environmental friendliness, independence of petroleum import, and a stable price level [3]. According to the US Department of Energy, the cost of hydrogen production from biomass in 2009 was comparable with the cost of hydrogen production by natural gas steam reforming [4].

Typical biogas contains 55–70% CH₄, 27–44% CO₂, <1% H₂, and 3% H₂S. Hydrogen sulfide present in biogas deactivates catalysts; for this reason, before performing the reforming process, H₂S is removed using absorption or biochemical methods or chemisorption on zinc or iron oxides. The kinetics of biogas steam reforming is described in terms of four reversible reactions: two methane steam reforming reactions (1) and (2), carbon dioxide methane steam reforming (3), and the water–gas shift reaction (4) [5]:





$$\Delta H_{298\text{K}}^\circ = 247 \text{ kJ/mol},$$



$$\Delta H_{298\text{K}}^\circ = -41 \text{ kJ/mol}.$$

Reactions (1)–(3) are endothermic, so heat needs to be supplied for maintaining the necessary thermal conditions. Reaction (4) is exothermic, supplying a small amount of heat to the reaction zone. For increasing the reaction rate, it is necessary to raise the temperature and employ a catalyst.

Nickel catalysts are very active in the steam and carbon dioxide reforming of biogas and, owing to their low cost, are industrially widespread. However, there serious drawback is that they lose activity because of coking. Catalysts based on noble metals are less prone to carbon deposition, since they present a higher energy barrier to carbon formation than nickel [6]. There have been many works devoted to the kinetics of the steam and carbon dioxide reforming of methane over catalysts based on noble metals, such as rhodium and ruthenium. Jakobsen et al. [7, 8] studied the kinetics of the steam and carbon dioxide reforming of methane over Rh/ZrO₂ and Ru/ZrO₂ catalysts at 500–800 and 425–575°C. They used nitrogen -diluted mixtures (containing 5–85% nitrogen) for maintaining the isothermality of the process. It was demonstrated that steam methane reforming is a first-order reaction with respect to methane but depends on the rate of CO and H₂ adsorption on the catalyst surface. Wei and Iglesia [9] investigated the kinetics of the steam and carbon dioxide reforming of methane over Rh/Al₂O₃ and Rh/ZrO₂ catalysts containing 0.1 to 1.6 wt % Rh, including the effect of the size and degree of dispersion of Rh particles on the turnover number of the reaction. The steam and carbon dioxide methane reforming reactions were found to be first-order with respect to methane and zero-order with respect to water and carbon dioxide. It was also demonstrated that the water–gas shift reaction is at equilibrium over all Rh catalysts.

In biogas steam reforming, the steam and carbon dioxide methane reforming reactions proceed simultaneously under conditions of external heat supply. There have been only a few works dealing with the the simultaneous occurrence of reactions (1)–(4). For example, there have been experimental studies [5, 10] on the steam reforming of model biogas consisting of 60% methane and 40% carbon dioxide over commercial granular nickel catalysts in the temperature range from 600 to 900°C. The observed dependences of the biogas conversion and product concentrations on the reaction temperature and water : methane ratio are in good agreement with the corresponding equilibrium dependences. The authors of those studies claim that, at high temperatures, the dominant reaction is carbon dioxide methane reforming and the optimum temper-

ature for biogas steam reforming is 700°C. Avraam [11] has presented the most comprehensive experimental analysis of biogas steam reforming over a granular Ru/Al₂O₃ catalyst placed in the reformer tubes. It was investigated how the methane conversion and the hydrogen concentration in the synthesis gas depend on the feedstock composition and residence time.

In industry, biogas steam reforming is conducted in reformer tubes filled with a bulk catalyst. An alternative means of producing hydrogen is microchannel fuel processors [12], which are particularly important for distributed energy systems. Microchannel reactors involving small- and ultrasmall-size channels with a thin catalyst layer deposited on the inner surface of the microchannels are very promising for hydrocarbon reforming. This is due to the fact that the effective transfer length decreases with a decreasing channel width, eliminating external diffusion limitations to a considerable extent and allowing the chemical reactions involved in biogas steam reforming to be carried out at short residence times of down to 0.1 s. Microreactors are presently considered for use in the production of liquid fuel from synthesis gas via the Fischer–Tropsch synthesis [13].

Microchannel reactors are commonly fabricated using a large number of microstructured plates. Depositing a thin catalyst layer onto the microchannel surface instead of placing the catalyst in the microchannel space reduces pressure loss and makes it possible to use a considerably smaller amount of catalyst, thus justifying the use of noble metals [12, 14]. A possible variant of laboratory-scale microreactor is an annular microchannel whose walls contain a deposited thin film of a catalyst. This reactor allows one to regulate the catalyst temperature and to find the feedstock reforming conditions ensuring a high synthesis gas output rate, which is necessary for developing a fuel processor employing microstructured plates.

Here, we report an experimental study of the catalytic steam reforming of a model biogas consisting of 60% methane and 40% carbon dioxide over a rhodium catalyst in an annular microreactor at varied water : biogas ratios. Measurements were performed for a feed residence time of 0.12 s and reactor temperatures of 750 and 860°C. The catalyst temperature and the range of water : biogas molar ratios maximizing the specific hydrogen yield were determined.

EXPERIMENTAL

Experimental setup. The experimental study of biogas reforming into synthesis gas in a steam medium was carried out in an annular microreactor with a thin catalyst layer deposited on the surface of the internal cylindrical cartridge. The microreactor is schematized in Fig. 1. The internal cylindrical cartridge, made from refractory alloy KhN80, had an outer diameter of 6 mm and a length of 40 mm. The cylinder, coated with a 25-μm-thick catalytic layer, was pressed into an

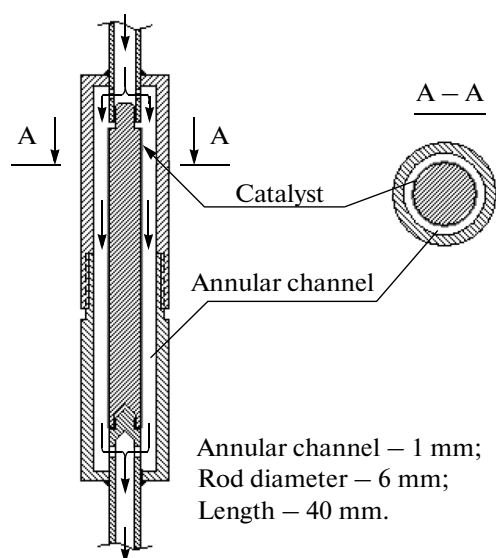


Fig. 1. Microreactor with an annular channel.

external, stainless steel, cylindrical tube with a wall thickness of 2 mm. This allowed heat to be supplied to the cylinder from the outer, heated wall of the reactor. The width of the annular channel in which the reaction mixture moved was 950 μm . The thickness of the channel walls ensured efficient heat transfer to the reaction zone, so biogas reforming proceeded under isothermal conditions. For heating the reactor to the preset temperature and for stabilizing the catalyst temperature, the reactor was placed in an electrically heated quartz tube covered with a heat-insulating layer for minimizing heat loss. The catalyst temperature was measured with a chromel/alumel thermocouple placed inside the cylindrical cartridge. For water evaporation and for premixing the feedstock gases, an electrically heated evaporator/heater was placed before the reactor. The feedstock was a model biogas consisting of methane, carbon dioxide, and water in different molar ratios ($\text{CO}_2/\text{CH}_4 = 0.66$; $\text{H}_2\text{O}/\text{CH}_4$ varied between 1.6 and 5.4). The gases were supplied using a mass flow controller (Bronkhorst HI-TECH). The experiments were performed at a pressure of 1.24 bar, a residence time of 0.12 s, and reactor temperatures of 750 and 860°C. The gas mixture leaving the reactor was passed through a cooler/condenser to remove water vapor and through a moisture trap, and the dry gas mixture was directed to a PerkinElmer 1016 gas chromatograph with a thermal-conductivity detector. The chromatograph was fitted with Hayesep T60/80, Hayesep N60/80, and Molecular Sieve 5A 45/60 columns, which made it possible to determine the following gases: hydrogen, carbon monoxide, carbon dioxide, methane, nitrogen, oxygen, acetylene, ethane, and ethylene. The carrier gases were helium and nitrogen. The volumetric flow rate of the dry gas mixture leaving the reactor was measured with a soap bubble

flowmeter. The volume fraction of water vapor was measured as the flow rate of condensed water. The chromatograph was calibrated using standard mixtures of methane, hydrogen, carbon monoxide, and carbon dioxide. The error in the measurement of the concentrations of the gas components of the mixture consisted of the error in the concentration measurements on the gas chromatograph, the error in the measurement of the volumetric flow rate of the dry mixture leaving the reactor, the error in the measurement of the flow rate of condensed water, and the error arising from the instability of the reactor temperature. The total error in the concentrations of the gases constituting the mixture was no larger than 10%.

For analyzing the results of our experiments, we determined quantities characterizing the reforming process and its efficiency. The methane and carbon dioxide conversions X_i in the reaction were determined via the formula

$$X_i = 1 - \frac{N_{i,SG}}{N_{i,BG}} = 1 - \frac{y_{i,SG}}{y_{i,BG} (y_{\text{CH}_4,SG} + y_{\text{CO}_2,SG} + y_{\text{CO},SG})}. \quad (5)$$

Here, N_i is the molar flow rate of gas i (methane or carbon dioxide) and y_i is the mole fraction of gas i in the gas mixture. The hydrogen yield was determined as the number of moles of hydrogen in the product mixture per mole of methane in the feedstock:

$$Y_{\text{H}_2} = \frac{N_{\text{H}_2,SG}}{4N_{\text{CH}_4,BG}} = \frac{y_{\text{H}_2,SG}}{4y_{\text{CH}_4,BG} (y_{\text{CH}_4,SG} + y_{\text{CO}_2,SG} + y_{\text{CO},SG})}. \quad (6)$$

Here, the hydrogen yield was normalized to the maximum possible number of moles of hydrogen that can result from 1 mol of methane via reaction (2). The residence time was determined as the ratio of the reactor volume to the flow rate of gas-vapor mixture consisting of biogas and steam under standard conditions (20°C, 1 bar): $\tau = V_r / (Q_{\text{BG},SC} + Q_{\text{H}_2\text{O},SC})$.

Catalyst preparation. The catalyst support was $\gamma\text{-Al}_2\text{O}_3$ with a specific surface area of 150–170 m^2/g , a high thermal stability, and a high mechanical strength. Alumina was impregnated with an aqueous solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ba}(\text{NO}_3)_2$. The amounts of the salts were adjusted so that the La_2O_3 and BaO content of the support was 2 and 3 wt %, respectively. The introduction of La_2O_3 and BaO markedly enhances the thermal stability of the catalyst, reduces the sintering rate, and slows down $\gamma\text{-Al}_2\text{O}_3$ transformation into other phases. The resulting suspension was dried and was then calcined at a high temperature to decompose the nitrates $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ba}(\text{NO}_3)_2$. The doped support was impregnated with an aqueous solution of $\text{Rh}(\text{NO}_3)_3$ so that the amount of pure metal was 5% of the support weight. The resulting catalyst was dried and was then calcined to decompose rhodium nitrate $\text{Rh}(\text{NO}_3)_3$ to small Rh_2O_3 particles. The sample obtained in this way

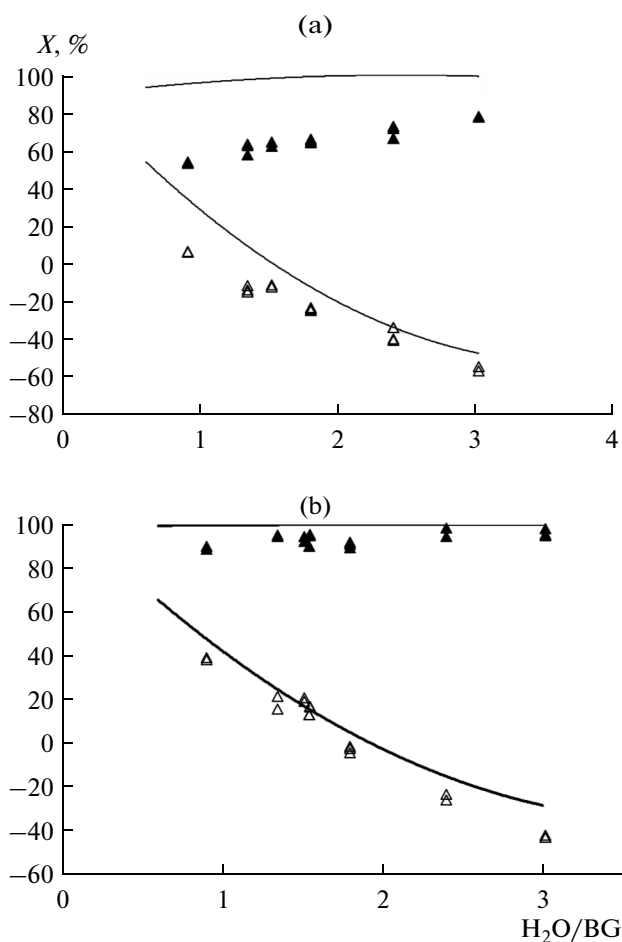


Fig. 2. Methane (solid symbols) and carbon dioxide (open symbols) conversions as a function of the water : biogas molar ratio for reactor temperatures of (a) 750 and (b) 860°C. The lines indicate the equilibrium conversions.

was characterized by electron microscopy. Electron micrographs were used to determine the particle size distribution, which demonstrated that the average size of rhodium particles is 1 nm. Prior to performing experiments, rhodium oxide was reduced with a hydrogen (5%) + nitrogen mixture for 3 h at a reactor temperature of 650°C to obtain rhodium metal.

RESULTS AND DISCUSSION

The temperature of the inner wall of the reactor (catalyst temperature) was maintained constant during a given run and varied within $\pm 3^\circ\text{C}$ from one run to another. The ratio of the water and biogas molar flow rates (H_2O/BG) was varied between 0.8 and 3. Figure 2 plots the methane and carbon dioxide conversions as a function of the H_2O/BG molar ratio for catalyst temperatures of 750 and 860°C. The conversions were determined via Eq. (5) using the mole fractions of the gases constituting biogas and synthesis gas. The points in Fig. 2 represent experimental data, and the lines

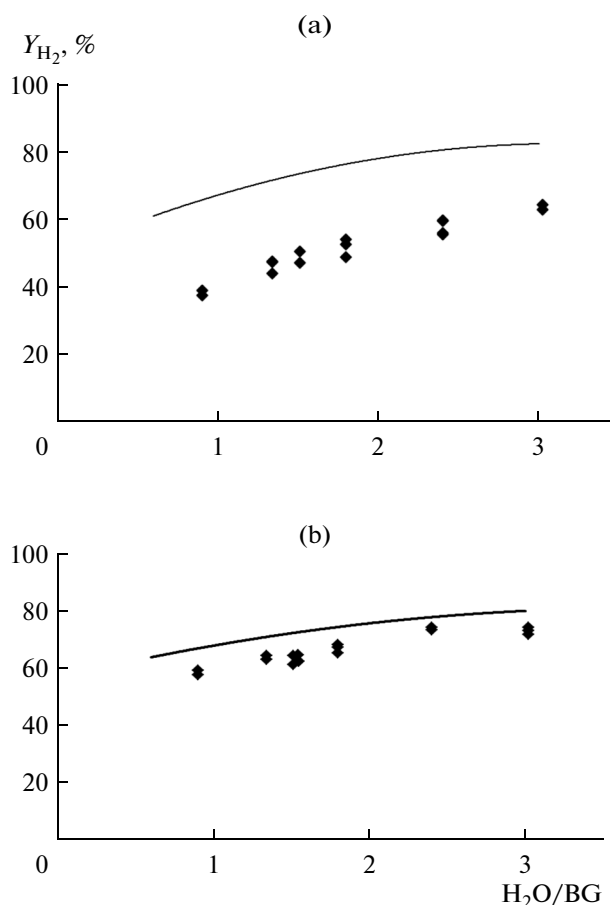


Fig. 3. Hydrogen yield as a function of the water : biogas molar ratio for reactor temperatures of (a) 750 and (b) 860°C. The lines indicate the equilibrium hydrogen yields.

indicate the equilibrium conversion values for these gases. Clearly, the methane and carbon dioxide conversions at 750°C depend on the H_2O/BG molar ratio (Fig. 2a). As H_2O/BG is increased, the methane conversion increases but remains far below its equilibrium value. The carbon dioxide conversion changes its sign at $H_2O/BG > 1$, indicating the onset of carbon dioxide buildup. Similar trends are observed at 860°C (Fig. 2b). At this temperature, carbon dioxide buildup begins at $H_2O/BG > 1.8$. The methane conversion at this temperature reaches 98% and is close to the equilibrium conversion. These data demonstrate that, for biogas reforming over the thin-layer rhodium catalyst at a residence time of 0.12 s, the reactor temperature should be at least 860°C. Carbon dioxide is consumed at this temperature when the H_2O/BG molar ratio is no larger than 1.8.

A study of the methane and carbon dioxide conversions for the carbon dioxide reforming of methane at an increased carbon dioxide flow rate such that $CO_2/CH_4 = 1.5$ showed that the synthesized catalyst displays a high activity in the carbon dioxide reforming of methane.

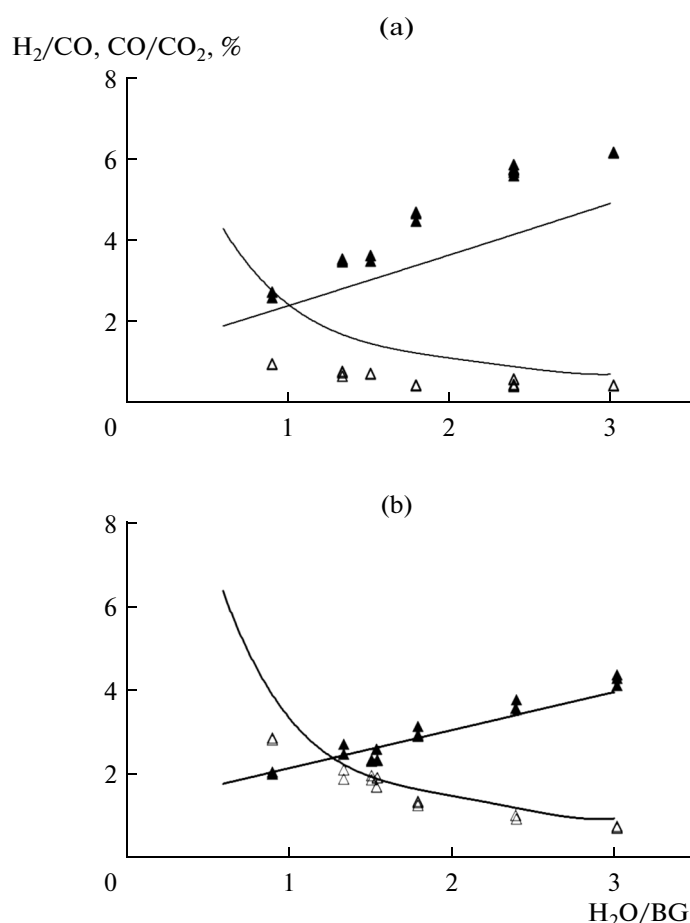


Fig. 4. Hydrogen : carbon monoxide (solid symbols) and carbon monoxide : carbon dioxide (open symbols) mole fraction ratios as a function of the water : biogas molar ratio for reactor temperatures of (a) 750 and (b) 860°C. The lines indicate the equilibrium mole fraction ratios.

Figure 3 shows how the hydrogen yield depends on the H_2O/BG molar ratio for catalyst temperatures of 750 and 860°C. The hydrogen yield was calculated via Eq. (6) using the mole fractions of the gases constituting biogas and synthesis gas. At 860°C, the hydrogen yield is close to its equilibrium value and increases slightly with an increasing H_2O/BG molar ratio. Figure 4 plots the hydrogen : carbon monoxide and carbon monoxide : carbon dioxide mole fraction ratios versus the H_2O/BG molar ratio for catalyst temperatures of 750 and 860°C. At 750°C, the ratios of the mole fractions of these gases are substantially smaller than their equilibrium values (Fig. 4a). At 860°C, the hydrogen : carbon monoxide and carbon monoxide : carbon dioxide mole fraction ratios are close to their equilibrium values (Fig. 4b). These data demonstrate that, at a reactor temperature of 860°C under high biogas conversion conditions, the H_2/CO ratio in the synthesis gas can be varied in a wide range (from 2 to 4.4), which is essential for a number of chemical technologies involving synthesis gas.

Note that the synthesis gas production capacity of the microreactor with a single annular channel (inner diameter of 6.05 mm, channel width of 950 μm) reaches 320 $m^3/(kg_{Cat} h)$, which is 30 times higher than the hydrogen production capacity of a reactor 47 mm in diameter filled with the commercial nickel catalyst KATALCO 57-4 [10].

CONCLUSIONS

We carried out an experimental study of the steam reforming of 60% methane + 40% carbon dioxide model biogas in a microreactor under isothermal conditions, with the reaction activated in a thin catalyst layer covering the inner convex wall of the annular microchannel. The experiments were performed at reactor temperatures of 780 and 860°C, a feedstock residence time of 0.12 s, and steam-to-biogas molar ratios of 0.9–3.1 in the feedstock. Under these conditions, the synthesized catalyst Rh/Al_2O_3 afforded a high biogas conversion at 860°C, at which the composition of the reforming products, including the hydrogen and carbon monoxide mole fractions were close to their equilibrium values. Carbon dioxide consumption at 860°C takes place when the H_2O/BG molar ratio is no larger than 1.8. Under high biogas conversion conditions, the H_2O/BG molar ratio in the resulting synthesis gas can be varied in the wide range from 2 to 4.4 by tuning the H_2/CO molar ration in the feedstock, which is essential for a number of chemical processes utilizing synthesis gas.

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NOTATION

ΔH —heat of reaction, kJ/mol;
 N —molar flow rate, mol/s;
 Q —volumetric flow rate, m^3/s ;
 V_r —reactor volume, m^3 ;
 X —conversion;
 Y_{H_2} —hydrogen yield;
 y —mole fraction of a gas in the mixture.

SUBSCRIPTS AND SUPERSSCRIPTS

BG —biogas;
 i — i th gas in the gas mixture;
 SG —synthesis gas;
 SC —standard conditions (20°C, 1 bar).

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